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THE EFFECT OF *TERT*-BUTANOL ON THE VACUUM ULTRAVIOLET PHOTOLYSIS OF PHENOL IN THE PRESENCE OF N_2O

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ABSTRACT

For the optimization of the water purifying technologies using advanced oxidation processes (AOPs), the accurate knowledge of the chemical mechanisms and the effect of different present components are needed. The aim of this study was to investigate the effect of *tert*-butanol (as a free radical scavenger) in various concentrations on the vacuum ultraviolet photolysis of phenol in presence of dinitrogen oxide (N_2O) as a radical transfer material to $^{\bullet}OH$ both e_{aq}^- and $H^{\bullet}$.
A Xe excimer lamp was used to irradiate the aqueous solution of phenol (10^{-4} mol L^{-1}) in the presence of dissolved N_2O and *tert*-butanol in 0.500, 0.050 and 0.001.mol L^{-1} concentrations. The degradation of phenol was followed using high performance liquid chromatography, and the formation of hydrogen peroxide (H_2O_2) from the reactions of reactive oxygen species was measured by UV spectrophotometer.
N_2O reacts with $H^{\bullet}$ and e_{aq}^- and transforms that to reactive $^{\bullet}OH$. Thus, the radical set includes mainly $^{\bullet}OH$ caused the degradation rate of phenol was significantly higher in the presence of N_2O than in absence it in oxygen free solution.
The *tert*-butanol as $^{\bullet}OH$ scavenger, decreased the degradation rate of phenol markedly in each concentration. The explanation of this experience is the formed less reactive radicals (carbon centred radicals form from *tert*-butanol) can not contribute to the degradation of phenol significantly. The *tert*-butanol addition also reduced the generation of H_2O_2, because of the reduced amount of $^{\bullet}OH$.

INTRODUCTION

The advanced oxidation processes (AOPs) are an important method for investigation, because effective degradation processes are needed to remove different organic contaminants (pesticides, medicines, etc.) from the waters. In these methods the transformation of the contaminants takes place in reactions with different reactive radicals (hydroxyl radical ($^{\bullet}OH$), hydrogen atom/hydrated electron ($H^{\bullet}/e_{aq}^-$), hydroperoxyl radical/superoxide radical anion ($HO_2^{\bullet}/O_2^{\bullet-}$)). The most important radical is $^{\bullet}OH$ due to its high reactivity and low selectivity [1]. $^{\bullet}OH$ can be generated by different processes, one of them is the vacuum-ultraviolet (VUV) photolysis. During this method the water molecules are irradiated with VUV photons with a wavelength shorter than 200 nm (in this case 172 nm, generated by Xe excimer lamp).

$$H_2O + h\nu_{172\ nm} \rightleftharpoons H^{\bullet} + {}^{\bullet}OH \qquad \Phi^{\bullet}_{OH}{}^{172\ nm} = 0.42\ [2]$$

$$H_2O + h\nu_{172\ nm} \rightarrow H^+ + e_{aq}^- + {}^{\bullet}OH \qquad \Phi_{eaq^-}{}^{172\ nm} < 0.05\ [1]$$

During the VUV photolysis the generated primary radicals are $^{\bullet}OH$ and $H^{\bullet}$ (e_{aq}^- is generated only in low concentration), their recombination is very favourable because of the 'cage effect' [3]. When other components also are present in the solution, they compete with the target molecule for the radicals, reducing the degradation rate. These compounds are generally called radical transfers, because these result in radicals too during their reactions. If the reactivity of the formed radicals towards the target compound is negligible, the radical transfer behaves as a radical scavenger.
In this study the *tert*-butanol was chosen as a radial scavenger molecule to investigate the effect of its various concentrations on the efficiency of VUV photolysis of phenol. During our experiments N_2O was applied also as a radical transfer to transfer $H^{\bullet}/e_{aq}^-$ to $^{\bullet}OH$.

MATHERIALS and METHODS

Materials, experimental setup and reaction conditions

During our experiments 250 ml aqueous phenol (VWR, 100.0%) solutions ($c_0 = 1.0\times10^{-4}$ mol L^{-1}) were irradiated by a Xe excimer lamp (Radium Xeradex^{TM}, 20 W electrical input power) emitting VUV photons (172 ± 14 nm wavelength). The solutions were bubbled with N_2O gas, with a flow rate of 600 ml min^{-1} before and throughout the irradiation. The samples contained *tert*-butanol (VWR, 100.0%) in 0.500; 0.050 or 0.001 mol L^{-1} concentration. The solutions were circulated with a peristaltic pump between the stirred reservoir and the reactor (thermostated at 25 ± 0,5 °C) with 375 ml min^{-1} flow rate. The kinetic investigation were started by switching on the lamp.

Analytical methods (HPLC, UV-spectrophotometer)

The concentration of phenol was followed by high performance liquid chromatography, using an Agilent 1100 chromatograph with LiChroCART 150-4.6, RP-19 column with 5 µm particle size. The mobile phase was 35% methanol (VWR 99.80%) and 65% ultra pure water (MILLIPORE Milli-Q Direct 8/16). 20 µl samples were analyzed, with 0.800 ml min^{-1} eluent flow rate at 25 °C, and the detection wavelenght of 210 nm.
The generation of H_2O_2 was followed using the Wasserstoffperoxid-Test produced by Merck by spectrophotometry. The special test is based on the reduction of Cu(II) to Cu(I), which forms a coloured complex with phenanthroline. This complex was analysed with the Agilent 8453 UV-VIS spectrophotometer, the detection wavelength of 455 nm.
The changes of pH of the solutions were followed using an IonLab pH 730p pH-meter, set to automatic measuring mode.

RESULTS

The effect of N_2O

First of all, the effect of N_2O on the transformation rate of phenol was determined by bubbling the solutions with this gas. Dissolved N_2O reacts with $H^{\bullet}/e_{aq}^-$ and transfers it to $^{\bullet}OH$.

$N_2O + e_{aq}^- \rightarrow N_2 + O^-$ $\quad k_1 = 7.0\times10^9$ L mol^{-1} s^{-1} [4]

$O^- + H_2O \rightarrow OH^- + {}^{\bullet}OH$ $\quad k_2 = 7.9\times10^7$ L mol^{-1} s^{-1} [4]

$N_2O + {}^{\bullet}H \rightarrow N_2 + {}^{\bullet}OH$ $\quad k_3 = 2.1\times10^6$ L mol^{-1} s^{-1} [5]

Consequently, the concentration of the reactive $^{\bullet}OH$ increases and the recombination of primary radicals is hindered in presence of N_2O.

$^{\bullet}OH$ + phenol →dihydroxy cyclohexadienil radical $\quad k_4 = 6.6\times10^9$ L mol^{-1} s^{-1} [6]

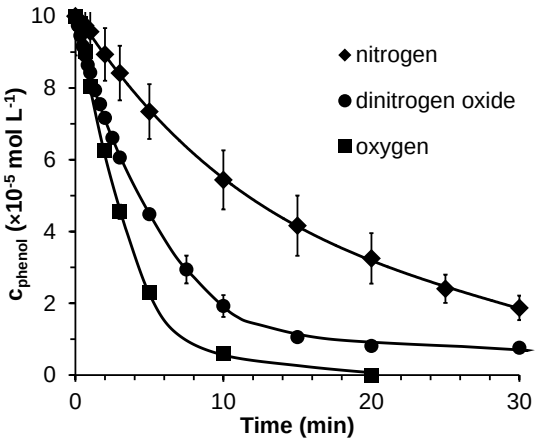
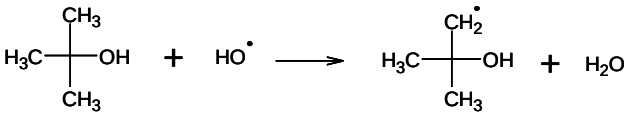


Fig. 1 Kinetic curves of phenol in solution saturated with N_2O, O_2 and oxygen free solution during vacuum ultraviolet photolysis

In oxygen free solutions (bubbled with nitrogen gas) the recombination of the primary radicals is more favourable, thus the degradation rate of phenol was moderate. *Fig. 1* shows that in N_2O or O_2 saturated solutions the phenol degradation rate was found to be significantly higher (an increase by 30 %) than in absence of these radical transfers. The explanation of this experience is the increase of $^{\bullet}OH$ concentration in the solution caused by the reactions of N_2O and O_2.

The effect of *tert*-butanol

The *tert*-butanol was used as a radical scavenger in solutions saturated with N_2O, to model the effects of alcohols on the AOPs. The *t*-BuOH reacts with $^{\bullet}OH$ (k_5) with large reaction rate (the *t*-BuOH concentration is relatively large) and forms 2,2-dimethyl-2-hydroxyethyl carbon centred radical, which does not react considerably with phenol.



$k_5 = 6.0\times10^8$ L mol^{-1} s^{-1} [6]

On the other hand, *t*-BuOH can react with $H^{\bullet}/e_{aq}^-$ also, however only with a three orders of magnitude lower rate constant (1.7×10^5 L mol^{-1} s^{-1} and 4×10^5 L mol^{-1} s^{-1} [6]). The degradation rate of phenol decreased significantly in the presence of *t*-BuOH (*Fig. 2*). The effect of *t*-BuOH was found to be more remarkable with increasing its concentration. This material reduces the concentration of $^{\bullet}OH$ and does not transform to radicals which could contribute to the decomposition of phenol.

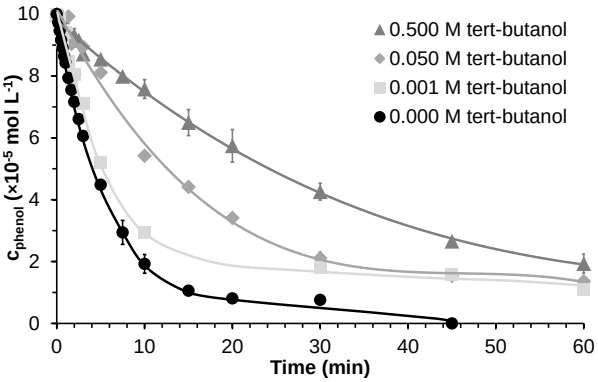


Fig. 2 The effect of *t*-BuOH on the degradation of phenol in solutions saturated with N_2O during vacuum ultraviolet photolysis

In the presence of *t*-BuOH the rate of accumulation of H_2O_2 also decreases (*Fig. 3*), because of the decrease of the concentration of $^{\bullet}OH$ and the absence of other reactive oxygen containing radicals.

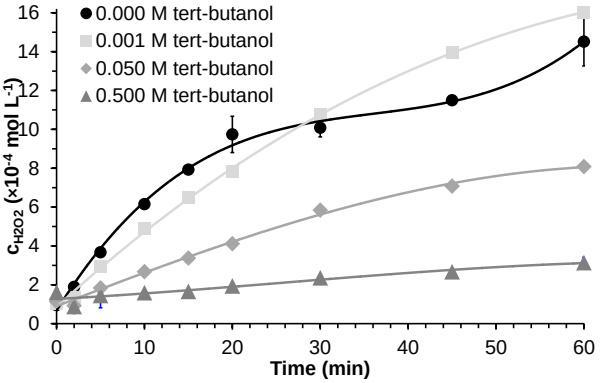


Fig. 3 The effect of *t*-BuOH on the H_2O_2 formation in the presence of N_2O during vacuum ultraviolet photolysis of phenol

CONCLUSIONS

- In the present work the effects of N_2O and the various concentrations of *tert*-butanol were investigated during the vacuum ultraviolet photolysis of phenol.
- The dissolved N_2O significantly increased the rate of transformation of phenol.
- Addition of *tert*-butanol decreased both the rate of transformation of phenol and the rate of accumulation of H_2O_2.
- Both effects can be explained by the decrease of the concentration of $^{\bullet}OH$ due to the addition of *t*-BuOH, and the absence of the reactive oxygen contained radicals.

ACKNOWLEDGEMENT

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